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Self-assembly in mixtures of amphiphilic polymers and surfactants

H. Diamant and D. Andelman

School of Physics and Astronomy
Raymond and Beverly Sackler Faculty of Exact Sciences
Tel Aviv University, 69978 Tel Aviv, Israel

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Abstract. – We present a model for the joint self-assembly of amphiphilic polymers and small amphiphilic molecules (surfactants) in a dilute aqueous solution. The polymer is assumed to consist of a hydrophilic backbone and a large number of hydrophobic side groups. Preference of the surfactant to bind to hydrophobic microdomains along the polymer induces an effective attraction between bound surfactants. This leads to two distinct binding regimes depending on a single physical parameter, ϵ, which represents the ratio between surfactant-polymer affinity and polymer hydrophobicity. For small ϵ the binding is non-cooperative, whereas for large ϵ it becomes strongly cooperative at a well-defined critical aggregation concentration. Our findings are in accord with observations on diverse experimental systems.

A considerable experimental and theoretical effort has been devoted in recent years to the study of mixtures of polymers and amphiphilic molecules (surfactants) in solution [1]. Of particular interest and importance are systems where the polymer itself has amphiphilic qualities as they exhibit rich self-assembly behaviour [2]. These systems offer, on one hand, numerous industrial applications, since their properties (*e.g.,* rheology) can be conveniently tuned and their solubility in water makes them "environmentally friendly". On the other hand, their complex amphiphilic nature poses a challenge to current theoretical investigations far beyond more conventional polymers in solution. Besides industrial applications, biological macromolecules, such as proteins, RNA and single strands of DNA, may be viewed as special, more complex cases of amphiphilic polymers.

In the current work we focus on the case where a large fraction of hydrophobic side groups are chemically attached to a hydrophilic polymer backbone (fig. 1a). The properties of such macromolecules and their interaction with free surfactants in solution have been investigated in a series of experiments during the past years, revealing rich self-assembly behaviour [3, 4]. One of the notable findings is that the cooperativity of the surfactant-polymer binding, which is related to interactions between bound surfactants, sensitively depends on the polymer properties (*e.g.,* its hydrophobic side chains and the degree of ionisation of its backbone). Previous

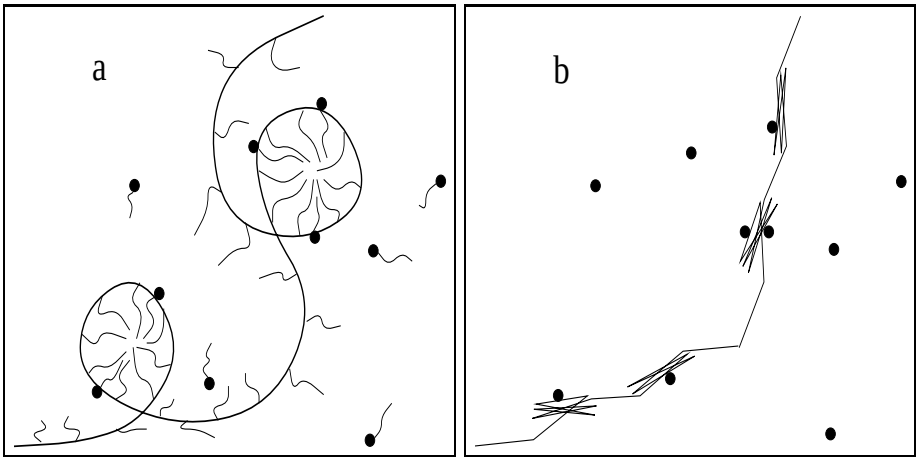

Fig. 1. – (a) Schematic view of a section of a side-chain amphiphilic polymer with bound surfactants. (b) Schematic view of the system as described by our model.

theories treating polymer-surfactant mixtures [5, 6, 7] did not address the diverse behaviour of those experimental systems. Our aim in this Letter is to construct a simple model which yields a qualitative understanding of the thermodynamics of such systems while accounting, in particular, for the polymer-induced interactions between bound surfactants. We neglect, therefore, structural details such as the size of the hydrophobic side chains, steric effects, chain rigidity etc., which are microscopically important but not expected to qualitatively affect the thermodynamics. A more refined model, including structural details, has allowed us to verify this assumption and will be presented in a future paper [8]. Transmission Electron Micrographs of dilute solutions of side-chain amphiphilic polymers, with and without surfactant, show self-assembled hydrophobic microdomains forming locally along the polymeric chains, while the chains seem to maintain overall extended conformations [4]. This observation is explained by the highly hydrophilic polymer backbone (usually a polyelectrolyte) and the high density of hydrophobic side groups along the chain. We are allowed, therefore, to consider only local association along the chain sequence, which greatly simplifies the model. The current work is restricted to the dilute limit, where inter-chain effects can be neglected and the surfactant is below its critical micelle concentration, in accordance with the relevant experiments.

Consider a flexible chain of N segments in contact with a surfactant reservoir of chemical potential $\mu_{\rm s}$. To each segment we assign a vector, $\mathbf{u}_n$, and denote the number of surfactants bound to it by φ_n. The energy gained by a segment joining a microdomain is denoted by α, and the one gained by a surfactant bound to such a microdomain is γ. The energetic parameters, α and γ, represent, respectively, measures of the polymer hydrophobicity and polymer-surfactant affinity. (All energies in this Letter are in units of $k_{\rm B}T$.) The partition function for the polymer-surfactant system is

$$\begin{aligned} Z_{\rm ps} &= \operatorname*{Tr}_{\{\varphi_n\}} \int \mathcal{D}\mathbf{u}_n \exp(-\mathcal{H}_{\rm ps}/k_{\rm B}T) \\ \mathcal{H}_{\rm ps}/k_{\rm B}T &= \sum_{n=1}^{N} \lambda_n u_n^2 - \sum_{n=1}^{N-1} \frac{\alpha+\gamma\varphi_n}{4}(\mathbf{u}_{n+1}-\mathbf{u}_n)^2 - \mu_{\rm s}\sum_{n=1}^{N}\varphi_n \end{aligned} \qquad (1)$$

where the λ_n are Lagrange multipliers ensuring the constraints $\langle u_n^2\rangle = 1$ ($\langle\cdots\rangle$ denotes a

thermal average over all chain configurations). Some of our results can be more easily derived imposing infinitely stiff segment constraints ($u_n^2 = 1$). Yet, other results, in particular the effect of polymer configurations on surfactant binding, cannot be obtained as easily using such an approach. We have modelled the association property of the polymer by a local tendency of the segments to fold, and the preference of the surfactant to join such clusters by a linear coupling to this folding [9]. Not explicitly included in eq. (1), interactions between surfactants may arise only indirectly through the coupling to chain configurations. Note that the current model contains no structural parameters. The hydrophobic microdomains are described as featureless clusters of folded polymer segments attracting free surfactants, as illustrated in fig. 1b. In a more refined model, steric and other repulsive effects should compete with the association, resulting in a finite radius of curvature for the microdomains [8]. Such microscopic details, however, do not alter the thermodynamic behaviour which concerns us in this work.

In the surfactant-free case, the partition function (1) becomes similar to the one for semi-flexible polymers [10],

$$Z_{\rm p} = \int \mathcal{D}\mathbf{u}_n \exp[-\sum_{n=1}^{N} \lambda_n u_n^2 + \frac{\alpha}{4} \sum_{n=1}^{N-1} (\mathbf{u}_{n+1} - \mathbf{u}_n)^2] \tag{2}$$

Yet, because of the tendency of segments in our model to *anti*-align ($\alpha > 0$), we need first to integrate over the "sub-lattice" $\mathbf{u}_2, \mathbf{u}_4, \ldots$ before taking the continuum limit. In addition, we replace all λ_n with a single λ. (This approximation amounts to a non-extensive correction in the free energy, which becomes negligible for $N \to \infty$ [8].) The resulting expression is

$$Z_{\rm p} = \left(\frac{\pi}{\lambda - \alpha/2}\right)^{3N/4} \int \mathcal{D}\mathbf{u}(n) \exp[-\frac{\tilde{\alpha}}{2} \int_0^N \left(\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}n}\right)^2 \mathrm{d}n - \frac{\tilde{\lambda}}{2} \int_0^N u^2(n) \mathrm{d}n] \tag{3}$$

where $\tilde{\lambda} \equiv \lambda(\lambda - \alpha)/(\lambda - \alpha/2)$, $\tilde{\alpha} \equiv \alpha^2/4(\lambda - \alpha/2)$, and $n : 0 \to N$ is now a continuous parameter along the chain. (Note that the continuum limit implies a large $\tilde{\alpha}$ and, hence, a large α.) The path integral in eq. (3) is readily evaluated using an analogy with a three-dimensional quantum oscillator [11] and the ground-state dominance [12], yielding

$$Z_{\rm p} = \left(\frac{\pi}{\lambda - \alpha/2}\right)^{3N/4} \exp\left[-(3N/2)\sqrt{\tilde{\lambda}/\tilde{\alpha}}\right] \tag{4}$$

Imposing now the constraint on $\langle u_n^2 \rangle$, $-\partial \log Z_{\rm p}/\partial\lambda = N$, we find $\lambda = \alpha + \mathrm{O}(1/\alpha)$, $\tilde{\lambda} = 9/2\alpha + \mathrm{O}(1/\alpha^2)$, and $\tilde{\alpha} = \alpha/2 + \mathrm{O}(1/\alpha)$. The correlation between alternating segment directions along the chain is found from eq. (3) as

$$\langle \mathbf{u}(n) \cdot \mathbf{u}(n') \rangle = \exp(-|n - n'|/\xi), \quad \xi = \alpha/3 \tag{5}$$

The value of ξ defines a chain length over which alternating segment directions, $\mathbf{u}_n, \mathbf{u}_{n+2} \ldots$, are correlated. Since the other segments within this length, $\mathbf{u}_{n+1}, \mathbf{u}_{n+3} \ldots$, are assumed, on average, to be anti-aligned with those vectors, we identify ξ as the average number of segments in a single folded cluster (see fig. 1b), *i.e.,* in a single hydrophobic microdomain. Thus, only when α is significantly large does the polymer tend to form microdomains by itself. The free energy of the chain is

$$F_{\rm p}(\alpha) = -\ln Z_{\rm p} - \lambda N = N[-\alpha + (3/4)\log(\alpha/2\pi)] \tag{6}$$

and can be viewed as composed of competing curvature energy (decreasing with α) and entropy (increasing with α) terms.

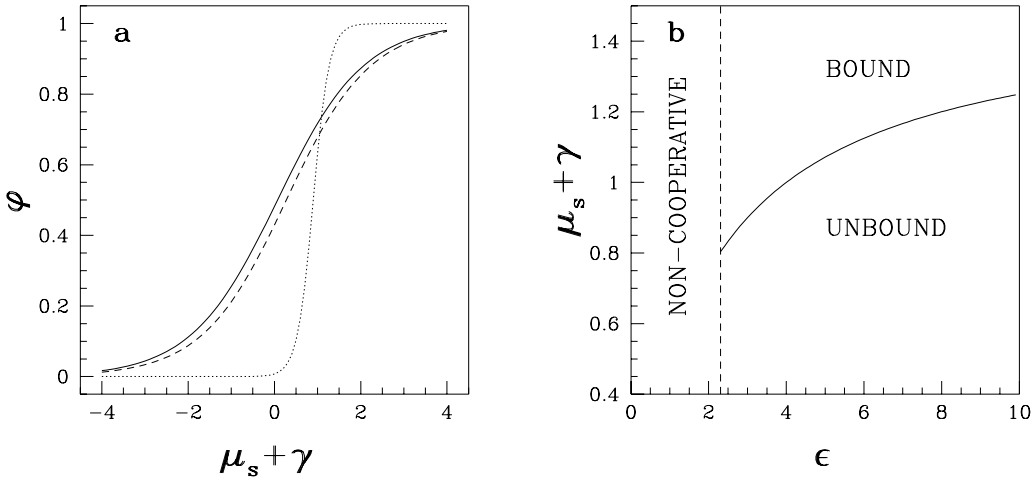

Fig. 2. – (a) Surfactant-polymer binding isotherms. Non-cooperative binding is shown for $\epsilon = 0.1$ (solid) and 0.5 (dashed) using eq. (8); cooperative binding is presented for $\epsilon = 3$ (dotted) using eq. (12). (b) Diagram presenting the surfactant-polymer binding behaviour. The dashed line separates two binding regimes: for small ϵ the binding is non-cooperative, whereas for large ϵ the binding is cooperative and exhibits a sharp (though continuous) increase at the *cac*. The values of $\mu_{\rm s} + \gamma$ corresponding to the *cac* are represented by the solid line.

We now return to the full polymer-surfactant partition function (1). For simplicity let us assume that at most one surfactant can bind to a monomer, *i.e.,* φ_n is either 0 or 1. Tracing over $\{\varphi_n\}$ and expanding to 2nd order in $\epsilon \equiv \gamma/\alpha$, we find the following expression for the free energy:

$$\frac{F_{\rm ps}}{N} \simeq \frac{F_{\rm p}}{N} + \ln(1-f) + \frac{3}{4} f\epsilon - \frac{3}{32} f(3+f)\epsilon^2 \tag{7}$$

where $f \equiv [1 + {\rm e}^{-(\mu_{\rm s}+\gamma)}]^{-1}$ is the average fraction of bound surfactant if it had been simply attracted to the polymer without coupling to its curvature. The first term in eq. (7) is the free energy of the surfactant-free chain, eq. (6), the second describes a regular lattice-gas contribution, and the remaining terms represent the surfactant-polymer interaction. From eq. (7) a binding isotherm can be calculated,

$$\varphi \simeq f[1 - (3/4)(1-f)\epsilon + (3/32)(1-f)(3+2f)\epsilon^2] \tag{8}$$

where φ is the average fraction of bound surfactant. Figure 2a shows two such isotherms (solid and dashed lines) for two different, small values of ϵ. In this regime the binding increases gradually with $\mu_{\rm s}$ (non-cooperative binding). For larger values of ϵ the isotherms are shifted to larger $\mu_{\rm s}$ and become steeper. Let us define a chemical potential, $\mu_{\rm s}^*$, for which the amount of bound surfactant is appreciable, *i.e.,* $\varphi = 1/2$. A corresponding cooperativity parameter is defined as $C \equiv \partial\varphi/\partial\mu_{\rm s}|_{\mu_{\rm s}^*}$. From eq. (8) we readily find

$$\mu_{\rm s}^* \simeq -\gamma + (3/4)\epsilon - (3/8)\epsilon^2 \tag{9}$$

$$C \simeq (1/4)[1 + (3/16)\epsilon^2] \tag{10}$$

The last, positive contributions to the average binding (8) and cooperativity (10) indicate an effective short-range attraction between bound surfactants induced by chain configurations. Once a molecule has bound to the chain, a folded hydrophobic region is formed, favouring binding of another molecule to the same region. Effective attraction is a general feature of annealed impurities. The important point, however, is that the attraction strength (resulting in binding cooperativity) depends on a single parameter, ϵ, denoting the ratio between surfactant-polymer affinity and polymer hydrophobicity.

For larger ϵ, the value of $\mu_{\rm s}^*$ can be estimated as

$$\mu_{\rm s}^* = -\frac{\gamma}{4}\langle(\mathbf{u}_{n+1}-\mathbf{u}_n)^2\rangle\Big|_{\varphi=1/2} = -\gamma + \frac{3\epsilon}{4(1+\epsilon/2)} \tag{11}$$

To obtain similar estimates for the binding isotherm and cooperativity we return to eq. (1) and make a cumulant expansion about the surfactant-free Hamiltonian *before* tracing over $\{\varphi_n\}$. Restricting to two-body interactions between nearest bound surfactants, the resulting partition function becomes analogous to a one-dimensional lattice-gas or Ising model with an attraction term proportional to ϵ^2. ([1]) Calculation of the binding isotherm and cooperativity is then straightforward and gives

$$\varphi = \frac{g[g-1+\sqrt{(g-1)^2+2h}]+h}{(g-1)^2+(g+1)\sqrt{(g-1)^2+2h}+2h};\quad g\equiv\frac{f}{1-f}{\rm e}^{-3\epsilon/4},\quad h\equiv 2g{\rm e}^{-3\epsilon^2/8} \tag{12}$$

$$C = (1/4)\exp[(3/16)\epsilon^2] \tag{13}$$

For small ϵ, eqs. (11)–(13) coincide with eqs. (8)–(10). Equation (13) is an important result since it demonstrates how sensitively the binding cooperativity depends on ϵ. In the regime of large ϵ the binding isotherm has a sharp (albeit continuous) slope at $\mu_{\rm s}^*$, as demonstrated by the dotted curve in fig. 2a. Hence, $\mu_{\rm s}=\mu_{\rm s}^*$ can be associated with $\phi_{\rm s}^*$, the so-called *critical aggregation concentration (cac)* of surfactant, $\mu_{\rm s}^*=\ln\phi_{\rm s}^*$.

Our findings are summarized in the diagram drawn in fig. 2b. Depending on the value of ϵ, two distinct binding regimes are predicted. The non-cooperative binding regime of small ϵ ($\alpha\gg\gamma$) corresponds to a situation where the surfactant almost does not affect the self-assembly of the polymeric side groups. The polymer is hydrophobic enough by itself to form microdomains and the bound surfactants merely join the already existing micelles, swelling them a little. On the other hand, the cooperative binding regime of large ϵ ($\gamma\gg\alpha$) corresponds to the opposite situation where the surfactant triggers the self-assembly. Above the *cac*, the number of repeat units per hydrophobic microdomain jumps from roughly α to about $\alpha+\gamma\gg\alpha$.

In recent experiments [3] both polymer hydrophobicity and surfactant-polymer affinity were changed by controlling the polymer charge and salt concentration (probably affecting both α and γ) and the length of the hydrophobic side chains (mainly affecting α). In those experiments the binding cooperativity could, indeed, be sensitively tuned by changing either the polymer hydrophobicity or its affinity to the surfactant, and the two distinct binding regimes described by our model were clearly observed.

Similar to regular surfactant micellisation, our self-assembly model yields a well-defined surfactant aggregation number determined by the correlation length of the polymer chain (the number of repeat units per microdomain) and the average fraction of bound surfactant. In our case of surfactant-polymer self-assembly, the aggregate size is restricted by the entropy of the

([1]) For large ϵ, many-body interactions among surfactants may become significant. Yet, since in our case all such contributions are attractive, they would merely enhance the binding cooperativity and further support our findings.

amphiphilic backbone, which imposes a finite correlation length along the chain. Moreover, like regular micellisation, the self-assembly at the *cac*, though sharp, is not a first-order transition. In our model this is due to the one-dimensionality of the effective interactions between surfactants.

We have presented a model which accounts for the experimentally observed diverse behaviour of dilute solutions of amphiphilic side-chain polymers and surfactants. Our results demonstrate the delicate balance in these mixed systems. By changing the parameters of the polymer and surfactant it is possible to cause aggregation and extensively modify the macroscopic properties of the solution. While capturing the thermodynamics of self-assembly in the system and accounting for the polymer-induced interactions between surfactants, our model still lacks the microscopic structural details required for a more complete description of the assembled microdomains themselves. Such a refinement will be presented in a future paper [8]. Another important extension of the model is to consider inter-chain association in more concentrated solutions and relate structural properties to rheological ones.

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